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^{15}N, ^{13}C and ^{1}H NMR spectra of three 2:1 cobalt(III) complexes of 1-(2-carboxyphenyl)azo-2-naphthol

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Abstract

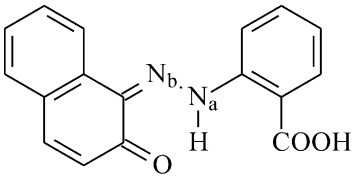
The ^{15}N, ^{13}C and ^{1}H NMR spectra of three 2:1 cobalt(III) complexes (**2a**–**c**) of 1-(2-carboxyphenyl)azo-2-naphthol (**1**) having the same elemental composition were measured in DMSO and analysed. It was found that the cobalt atom in all three compounds is six-coordinated, being bound to the two azo dye ligands via the two oxygens and the azo nitrogen originating from the anthranilic acid component of each azo dye. The compounds **2** differ in mutual space orientation of their ligands. In the green and bordeaux compounds, both ligands are equivalent (at least on the NMR time scale), whereas those in the olive compound are not.

Keywords: Cobalt(III)-azo dye complexes; ^{15}N NMR; ^{13}C NMR; ^{1}H NMR

1. Introduction

In previous papers [1–3], we investigated the 2:1 Co(III) and Al(III) complexes of some azo dyes. In all cases, only one reaction metallisation product was isolated and only one set of NMR signals for both ligands was observed, so providing evidence for their equivalence (at least on the NMR time scale). In contrast, Schetty and Kuster [4] reported the isolation of three components (**2a**–**c**) from the preparation of a 2:1 cobalt(III) complex of the dye (**1**) derived from coupling diazotised anthranilic acid to 2-naphthol.

In our previous papers [1–3,5–7] we demonstrated that NMR spectroscopy was a very sensitive probe for studying such compounds. The aim of this paper was to characterise the three 2:1 cobalt(III) complexes **2a**–**c** derived from the azo dye (**1**) by means of ^{15}N, ^{13}C and ^{1}H NMR, and to study their structures from the viewpoint of coordination at the cobalt atom and to compare the data with those published previously for analogous complexes.



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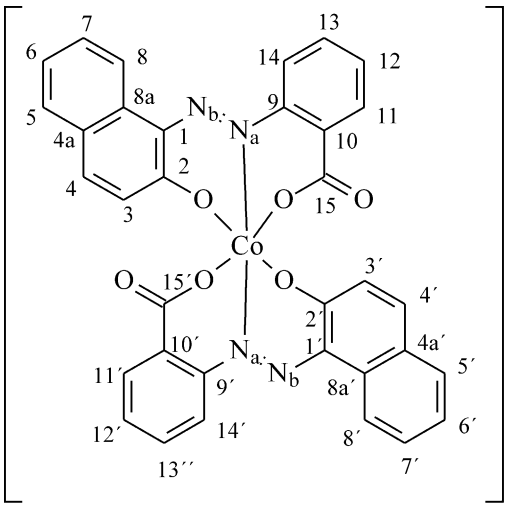

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2. Experimental

2.1. Synthesis

The compounds **2a**–**c** were prepared according to published procedure [4] from the precursor **1** and $CoSO_4 * 12H_2O$ and H_2O_2 in formamide solution. Three cobalt(III) complexes were isolated using column chromatography (Al_2O_3, methanol). The methanol was then evaporated in vacuo at ca. 25 °C.

The complexes labelled at N_b with ^{15}N (see structure **1** for designation of the N atoms) were prepared analogously in formamide solution using Na $^{15}NO_2$ (95% ^{15}N) for the preparation of dye **1**.

2.2. NMR spectroscopy

The ^{15}N (50.65 MHz), ^{13}C (125.76 MHz) and ^{1}H (500.13 MHz) NMR spectra of compounds **2a**–**c** were measured in hexadeuteriodimethyl sulfoxide at ambient temperature, using a Bruker Avance 500 spectrometer equipped with 5 mm broadband probe with *z*-shielding and a SGI O2 computer. The ^{15}N chemical shifts were referred to external neat nitromethane ($\delta(^{15}N) = 0.0$) and the ^{13}C and ^{1}H chemical shifts were referred to the central peak of DMSO-d_6 ($\delta(^{13}C) = 39.60$, $\delta(^{1}H) = 2.55$, respectively). Positive values of chemical shifts denote high frequency shifts with respect to standards.

Two-dimensional gs (gradient selected)-H,H-COSY, TOCSY, NOESY, 1D-gs-TOCSY, gs-HSQC, gs-HSQC–TOCSY and gs-HMBC [8,9] techniques were measured, using standard microprograms provided by Bruker [10].

3. Results and discussion

Schetty and Kuster [4] reported the preparation and isolation of three components in the 2:1 cobalt(III) complex of the dye (**1**), the latter being derived from the coupling of diazotised anthranilic acid to 2-naphthol. Several possible structures were proposed for these components, differing in the coordination of the second nitrogen of the azo group, and the presence of the ionised form of the carboxylic group. Schetty and Kuster [4] were unsuccessful in growing single crystals of these three components, because of their dynamic behaviour in solution. For example, a single chromatographically separated component gave a mixture of all three components after being dissolved in a solvent for some time. We decided to study these compounds by means of NMR spectroscopy.

The ^{15}N, ^{13}C and ^{1}H chemical shifts of three chromatographically isolated complexes **2a**–**c** measured in DMSO-d_6 are collected in Tables 1, 2. The ^{15}N, ^{13}C and ^{1}H chemical shifts of compound **1** were published previously in Ref. [3].

The ^{1}H and ^{13}C NMR spectra of the crude metallisation product from the dye **1** are complicated by strong overlap of signals from the three components. We prepared compounds **2a**–**c** that were selectively ^{15}N enriched at N_b. Fig. 1a shows the ^{15}N NMR spectrum of the $^{15}N_b$ selectively enriched crude metallisation product. Four ^{15}N resonances are clearly visible, the relative intensity ratio of signals depending on reaction conditions (especially the pH) and on the time after dissolving in DMSO. The crude product was chromatographed to give three components in line with Ref. [4], which were characterised by their colours:

Table 1
^1H, ^{13}C and ^{15}N NMR chemical shifts of compounds **2a**,**b** in DMSO-d_6

H/C No.		Bordeaux (**2a**)		Green (**2b**)	
		$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$	$\delta(^{13}C)$
1	1	–	134.78	–	140.09
2	2′	–	155.40	–	153.12
3	3′	6.59	123.00	6.21	121.97
4	4	7.61	137.13	7.43	137.04
4a	4a′	–	127.00	–	127.09
5	5′	7.75	128.55	7.75	128.58
6	6′	7.44	124.33	7.41	124.98
7	7′	7.71	128.67	7.60	128.71
8	8	8.59	121.35	8.03	120.27
8a	8a′	–	133.23	–	130.73
9	9′	–	149.79	–	150.12
10	10′	–	128.36	–	131.15
11	11′	8.16	131.75	8.12	130.62
12	12′	7.44	128.41	7.40	128.36
13	13′	7.77	131.75	7.10	130.48
14	14′	8.24	121.81	7.11	119.77
15	15′	–	167.21	–	168.91
N_a	$N_{a'}$	–	–93.0[a]	–	−106.8[a]
N_b	$N_{b'}$	–	65.1[a,b]	–	88.6[a,b]

[a] $\delta(^{15}N)$.
[b] ^{15}N selectively labelled compound.

Table 2
^1H, ^{13}C and ^{15}N NMR chemical shifts of compounds **2c** in DMSO-d_6

H/C No.	Olive (**2c**)		H/C No	Olive (**2c**)	
	$\delta(^1H)$	$\delta(^{13}C)$		$\delta(^1H)$	$\delta(^{13}C)$
1	–	139.70	1′	–	135.95
2	–	154.19	2′	–	156.45
3	6.32	122.44	3′	7.55	124.52
4	7.61	136.95	4	7.96	138.28
4a	–	127.79[a]	4a′	–	127.44[a]
5	7.81	128.55	5′	7.82	128.55
6	7.37	124.37	6′	7.46	124.93
7	7.48	128.10	7′	7.46	128.10
8	7.71[a]	120.28	8	7.61[a]	120.28
8a	–	[b]	8a′	–	[b]
9	–	150.21	9′	–	149.45
10	–	[b]	10′	–	[b]
11	8.12	131.14	11′	7.64	124.52
12	7.52	128.10	12′	7.50	128.10
13	7.48	128.10	13′	7.30	130.27
14	7.11	121.69	14′	7.02	120.07
15	–	169.90	15′	–	167.66
N_a	–	[c]	$N_{a'}$	–	C
N_b	–	89.3[d,e]	$N_{b'}$	–	80.5[d,e]

[a] Assignment can be interchanged within a line.
[b] 132.40, 131.20, 130.79 or 130.67.
[c] Not observed.
[d] $\delta(^{15}N)$.
[e] ^{15}N selectively labelled compound.

bordeaux, olive and green. The most intense ^{15}N NMR signal was given by the green component (Fig. 1b) whilst the intensities for the olive (Fig. 1c) and bordeaux (Fig. 1d) components were generally comparable, as can be seen from the ^{15}N NMR spectra of the chromatographically separated components. The spectra look very simple, but contain valuable information about the coordination of the nitrogen atoms [as indicated by $\delta(^{15}N)$ values] and the symmetry of the compounds (as indicated by the number of resonances). It is evident that in the green and bordeaux components, both ligands are equivalent (at least on the NMR time scale), while those in the olive complex are not. This conclusion is, of course, also supported by ^1H and ^{13}C NMR spectra (Tables 1 and 2).

The $^{15}N_b$ resonances could be assigned unambiguously, since ^{15}N selectively enriched compounds were used for the measurement of ^{15}N chemical shifts. The $^{15}N_a$ resonances were determined from ^{15}N NMR spectra measured for both the crude product and the separated components by long-term accumulation of ^{15}N NMR spectra.

The ^{15}N chemical shifts in compound 1 are as follows: $\delta(^{15}N_a) = -195.7$, $\delta(^{15}N_b) = -21.4$ (Ref. [3]). These values, as well as $^1J(^{15}N_a, H) = 93.0$ Hz, indicate clearly that compound **1** exists almost totally in the hydrazone form [11]. In previous papers [1–3,5–7] we reported on the application of ^{15}N NMR as a very sensitive technique for the detection of the existence of coordination as well for the determination of coordination position of nitrogens in –N=N– and –NH–N= groups, respectively.

Upfield ^{15}N chemical shifts of about 100 ppm are observed on protonation of various heterocyclic derivatives, for example, pyridine, purine, indolizine, etc. [12,13], where the nitrogen atom lone pairs are engaged in bonding to the proton. A similar effect ($\Delta\delta(^{15}N) = 102$–146 ppm) [6] is also typical of the coordination of a nitrogen atom of an azo dye to a metal ion, provided the dyes exist in azo form. On the other hand, such coordination

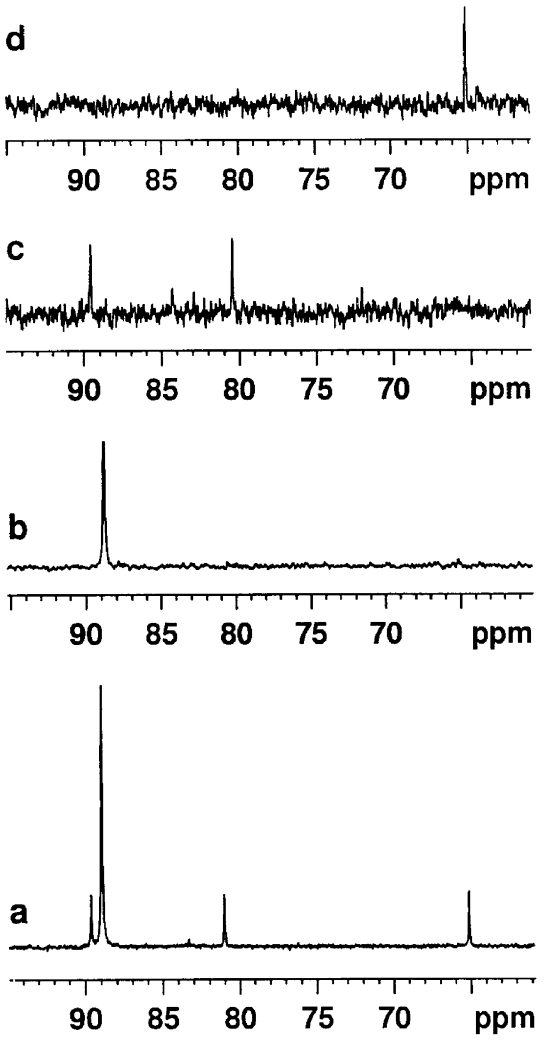

Fig. 1. ^{15}N NMR spectra of $^{15}N_b$ selectively enriched compounds **2**: (a) crude product, (b) green, (c) olive, and (d) bordeaux components.

can cause a relatively large *downfield* shift in the case where the ligand exists in the hydrazone form. Changes in $\delta(^{15}N)$ are due to a combination of two effects: the coordination (responsible for an *upfield* shift) and the change of the hydrazone tautomeric form to the azo form (responsible for even greater *downfield* shift). For additional details see Refs. [1–3].

On comparison of the data observed with analogous aluminium(III) compounds [3], it was clear that very similar ^{15}N chemical shifts also occurred with compounds **2a–c,** and this gives strong evidence for coordination of N_a, rather than N_b, with the cobalt atom in all three compounds. This conclusion is supported by the work of Jaggi [14], who carried out an X-ray analysis of the cobalt complex formed by coupling diazotised methylanthranilic acid to 1-(4-bromophenyl)-3-methylpyrazol-5one. Only one reaction product could be isolated, and he found that that in this complex, coordination of the cobalt atom also occurred with nitrogen N_a.

The ^1H and ^{13}C chemical shifts were assigned using gs (gradient selected)-H,H-COSY, TOCSY, NOESY, 1D-gs-TOCSY, gs (gradient selected)-HSQC (optimised for $^1J(^{13}C,H)$ ca. 160 Hz), gs-HSQC–TOCSY and gs-HMBC [11,12] (optimised for $^3J(^{13}C,H)$ ca. 5–10 Hz). Correlation of proton $H(11)$ with the carbon of the COO group in the HMBC spectra provided key information for the assignment of proton and carbon resonances C9–C14. The space proximity of protons $H(4)$ and $H(5)$ and/or the existence of appropriate cross-peaks via $^3J(^{13}C(4), H(5))$ and $^3J(^{13}C(5), H(4))$ in HMBC spectra were crucial for assignment of the naphthalene part of compounds **2a–c**. In the bordeaux (**2a**) and green (**2b**) components, both ligands are equivalent (at least on the NMR time scale) and the ^1H and ^{13}C chemical shift assignments were straightforward, using a set of two-dimensional NMR experiments. In the olive component (**2c**) both ligands are non-equivalent, and this overlapping NMR signals were obtained and signal assignment was much more complicated. Moreover, the chromatographic separation of the olive component was not easy, and variable amounts of both the green and bordeaux components were always present in the samples measured. The "connectivity" of the naphthalene and benzene parts of each particular ligand and the appropriate N_b nitrogen resonance was achieved by analysing the gs-^1H–^{15}N HMBC spectrum of the $^{15}N_b$ enriched compound. Due to ^{15}N enrichment and the resultant high sensitivity, weak cross-peaks via $^nJ(^{15}N,H)$ for $n \geqslant 4$ could be seen.

The ^{15}N chemical shifts values gave information about the coordination of the nitrogen atoms. It would be of great interest to measure ^{59}Co chemical shifts, but ^{59}Co has a 7/2 spin and a large

quadrupole moment and, thus, the NMR signals are usually very broad. In addition to this effect, the solubilities of compounds **2a**–**c** were rather low and thus we were unable to observe any ^{59}Co NMR signal. The ^{13}C chemical shifts of the COO groups provided additional information about the coordination. Thus the values of $\delta(^{13}C)(COO)$ in all three components were rather similar, indicating that Schetty and Kustner's proposal that the ligand component could have a free –COO group is improbable. We believe that the similarity of these ^{13}C chemical shifts strongly supports the fact that all carboxy groups are bound to the cobalt atom.

4. Conclusions

Compounds **2a**–**c** are isomeric, giving the same elemental analysis [4], and we found that in all three compounds the cobalt atom was six-coordinated, being bound to two azo dye molecules via the two oxygens and the nitrogen atom N_a (i.e. the one originating from the anthranilic acid diazo component) of each dye molecule. The complexes **2** must differ only in the mutual orientation of the ligands. In the green and bordeaux complexes, both ligands are equivalent (at least on the NMR time scale) while those in the olive complex are not. ^{15}N NMR spectroscopy proved to be the most important technique for the determination of the symmetry of the metallised azo dyes, and particularly for differentiation of the two nitrogen atoms of the azo group from the viewpoint of their involvement in coordination. Although NMR spectroscopy cannot provide as detailed a description of the space orientation of the two ligands in compounds **2a**–**c** as might X-ray analysis, NMR spectroscopy can nevertheless undoubtedly extend our knowledge about the structures of metallised azo dyes.

Acknowledgements

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